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Glycerol production and its applications as a raw material: A review

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ABSTRACT

Glycerol is a valuable byproduct in biodiesel production by transesterification, soap manufacturing by saponification as well as hydrolysis reaction. The purity of glycerol obtained is low due to the presence of impurities such as remaining catalyst, water, soaps, salts and esters formed during the reaction. Purification of glycerol as well as the conversion of glycerol into valuable products has attained growing interest in recent years due to the dramatic growth of the biodiesel industry. This paper reviews different methods of producing crude glycerol as the major by-product. Purification of glycerol was reported as well as value-added products produced from glycerol.

Contents

1. Introduction

Glycerol, also known as glycerine or propane-1,2,3-triol, is a chemical which has a multitude of uses in pharmaceutical, cosmetic, and food industries. It can be produced as a by-product from saponification and hydrolysis reactions in oleochemical plants as well as transesterification reaction in biodiesel plants [1]. Glycerol produced from oleochemical or biodiesel plant is in crude form that contains

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various impurities such as oily, alkali, and soap components, a salt or diols, depending on the processes and the type of materials processed [1,2]. It is normally referred to as crude glycerol. Crude glycerol obtained from the biodiesel plant consists of glycerol, water, organic and inorganic salts, soap, alcohol, traces of glycerides and vegetable colour [3]. While crude glycerol produced from the hydrolysis reaction contains glycerol, water, free fatty acid, unreacted triglycerides, organic and inorganic salts and matter organic non-glycerol [1]. For the reaction of saponification of fats or oil, crude glycerol has been reported to contain glycerol, fatty acids and salts [4]. Further crude glycerol is a low value product as its low purity limits its application as feedstock in industries. The development of conversion processes for crude glycerol to other value-added products is being thoroughly investigated; however, the techniques are not widely commercially adopted in Malaysia at present. Purified glycerol can be sold as a commodity because it is still highly required as an important industrial feedstock especially in various chemical industries. Consequently, a development of purification methods is necessary to produce highly purified glycerol as feasible industrial feedstock [5].

Presently, numerous purification techniques of crude glycerol have been developed such as conventional filtration, microfiltration, and ultrafiltration using organic polymer membranes, simple distillation, vacuum distillation, chemical and physical treatments, ion-exchange technique and adsorption. By combining two or more of these techniques would lead to higher purify glycerol [6]. This paper reviews the methods employed to produce glycerol as well as the purification technologies.

2. Physical and chemical properties of glycerol

Glycerol is an organic compound and it has the chemical formula $C_3H_8O_3$. It is synonymous to glycerine, propane-1,2,3-triol, 1,2,3-propanetriol, 1,2,3-trihydroxypropane, glyceritol, and glycyl alcohol. Glycerol is a low toxicity alcohol that consists of three-carbon chain with a hydroxyl group attach to each carbon. It is derived from natural or petrochemical feedstocks [7]. Glycerol is virtually nontoxic to both human and environmental. Physically, glycerol is a clear, colourless, odourless, hygroscopic, vicious and sweet taste liquid. The boiling point, melting point and flash point of glycerol is 290 °C, 18 °C and 177 °C respectively [8]. Under normal atmospheric pressure, glycerol has a molecular weight of 92.09 g/mol, a density of 1.261 g/cm^3, and a viscosity of 1.5 Pa.s [9]. The extensive intermolecular hydrogen bonding is responsible for high viscosity and boiling point of glycerol. Glycerol is able to attract and hold the moisture from the air and it is not altered when contact with the air [10]. The three-hydroxyl groups in glycerol dominate its solubility. It is completely soluble in water and alcohols, slightly soluble in ether and dioxane, but insoluble in hydrocarbon [9]. It is also a good solvent for many substances such as iodine, bromine and phenol due to the presence of the hydroxyl group. Glycerol is chemically stable under normal storage and handling conditions, nevertheless, it may become explosive when it is in contact with strong oxidizing agents such as potassium chlorate [10]. Glycerol is a reactive molecule that posses larger number of reactions due to the presence of primary and secondary alcoholic groups that can be replaced with other chemical groups. Furthermore, it undergoes various reactions to form other derivatives such as ether, ester, amine and aldehyde.

3. Source of glycerol

3.1. Transesterification reaction

Glycerol can be generated from transesterification of fat and oils in biodiesel plant. Transesterification is a chemical reaction whereby fat and oils (triglycerides) react with alcohol such as methanol in the presence of a catalyst to produce fatty acid methyl esters with glycerol as a byproduct, as presented in Fig. 1 [11]. The transesterification reaction is carried out in batch or continuous equipment. As the transesterification reaction progresses, the reaction stream is separated into two phases, which are biodiesel-rich phase (top layer) and glycerol-rich phase (bottom layer), due to differences in their densities and their polarities [12,13]. The production of 100 kg of biodiesel yields approximately 10 kg of impure glycerol, with purity of 50–55% [4]. Glycerol from the transesterification process has a higher salt content and excess alcohol. Today, the production of glycerol by transesterification of fats and oils in biodiesel industry has become a major source of glycerol production. However, the dramatic growth of the biodiesel industry has created a surplus glycerol that has resulted in decreasing glycerol prices and environmental concerns associated with contaminated glycerol disposal [14].

To produce biodiesel, a feedstock that contains fat or oils (triglycerides) can be used in the transesterification process. Ahmad et al. [15] stated that the cost of feedstock accounts for about 75% of the total cost of biodiesel production, thus, the selection of proper feedstock is important to ensure the low biodiesel production cost. In general, biodiesel feedstock can be categorized into three groups: first generation, second generation and third generation biodiesel feedstock as shown in Table 1. Enamul Hoque et al. [16] have produced biodiesel from used cooking oil and animal fat via transesterification process. At optimum conditions (methanol to oil ratio of 6:1, catalyst concentration of 1.25 wt% of oil, reaction temperature of 65 °C and stirring speed of 150 rpm), the maximum biodiesel yields achieved for beef fat, chicken fat and used cooking oil are 87.4%, 89% and 88.3%, respectively. The authors concluded that economically viable biodiesel could be produced from low cost feedstock through appropriate setting of process parameters in transesterification process. Miao and Wu [17] produced biodiesel from microalgae lipids using sulphuric acid as a catalyst via transesterification process. At optimum conditions (temperature of 30 °C and 56:1 M ratio of methanol), the best biodiesel yields were obtained in about 4 h of reaction time. Moazami et al. [18] estimated that 60,000 L of biodiesel could be produced from microalgae strain PTCC 6016 (Nanochloropsis sp.). However, despite of which feedstock is used to produce biodiesel, the by-product (glycerol) will be generated in the homogeneous or heterogeneous catalysed transesterification process. Asad-ur-Rehman et al. [35] investigated the crude glycerol produced from biodiesel production via transesterification of sunflower oil. The authors mixed the solution of methanol and sunflower oil (methanol: sunflower oil molar ratio of 10:1) at 400 rpm and 60 °C with 0.5% (w/w) of NaOH. The crude glycerol obtained have the following composition (w/w): 30% glycerol, 50% methanol, 13% soap, 2% moisture, approximately 2–3% salts (primarily sodium and potassium), and 2–3% other impurities (non-glycerol organic matter). Thompson and He [36] reported the characterization of crude glycerol obtained from different seed oil via a transesterification process. The transesterification process was conducted at 50 °C and at 240 rpm for 60 min using sodium methylate as catalyst. They reported that crude glycerol produced from the different types of feedstock is ranged between 60 wt% and 70 wt%. The results also showed that the crude glycerol yield for first-use oils ranged from 8.8 to 12.3 g per 100 g of input oil (~62 wt%). On the other hand, crude glycerol obtained from waste vegetable oil contain more soaps and impurities, average around

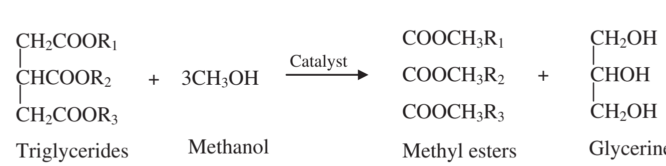


Fig. 1. Transesterification reaction.

Table 1
Current feedstock for biodiesel production.

Feedstock	Types	Remarks
First generation	Palm oil [19] Rapeseed [19,20] Soybean oil [21] [22] Sunflower oil [20] [23] Peanut oil [19]	– Known as food feedstock [15] – These oils are limited and caused the competition with the edible oil market [25] – High impact on food markets and security. [30] – Negative environmental impact as large portions of land were required to plant the biodiesel crops [15]
Second generation	Jatropha oil [24] Sea mango [25] Tobacco seed oil [26] Salmon oil [27] Waste cooking oils [19] Tallow [21]	– Reduced competition for food and feedstock [11] – Environmentally friendly as less farmland are required [31] – Poor performance in cold temperature [15] – The use of animal fats brings a biosafety issue as they may obtain from contaminated animals [32]
Third generation	Microalgae [15,18,28,29]	– Fast reproduction as they are easier to cultivate [28] – Economic, renewable and carbon neutral source of biofuel [18] – Enhanced cost efficiencies [15] – Environmentally friendly as microalgae do not compete for farmland with crops and capable of fixing carbon dioxide in the atmosphere [33] – Produce valuable by-product such as biopolymers, proteins [34]

22 g per 100 g of input oil (~76.6 wt%). Sharif Hossain et al. [37] conducted experimental studies on biodiesel production from algae (*Oedogonium* and *Spirogyra*) to investigate the amount of biodiesel produced and the physical properties (yield of biodiesel, glycerol and sediments) of the formed biodiesel. Their results show that biodiesel can be produced from both species of algae whereby more than 90% of biodiesel is obtained. However, the sediments (glycerol, water and pigments) generated after the transesterfication process was higher in biodiesel produced from *Spirogyra* than *Oedogonium*. Thus, the authors concluded that *Oedogonium* sp. is the better feedstock than *Spirogyra* to produce biodiesel via transesterification process.

The transesterification reaction requires a catalyst to split the oil molecules and an alcohol to combine with the separated esters as well as to boost the rate of the transesterification reaction [12]. Generally, the catalysts are acid, base or enzyme that is in homogeneous or heterogeneous form; depending on the amount of free fatty acid present in the oil [38]. Acid catalysts can be used if more water and free fatty acid are present in the triglycerides while alkali catalysts can be used if the triglyceride contains low free fatty acid content [39]. Homogeneous catalyst is a catalyst that remains in the same phase (liquid) as the reactants while the heterogeneous catalyst is the catalyst that remains in a different phase (solid, immiscible liquid or gaseous) to the reactants during the reaction [40]. Homogeneous catalysts lead to contamination and waste generation that making product separation and purification more costly whereas separation of heterogeneous catalyst from the product as well as regeneration and reutilization are easy to be carried out as it is insoluble in the product [41]. Table 2 summarizes the advantages and disadvantages of various types of catalyst used in transesterification reaction.

3.1.1. *Acid catalysed transesterification*

Acid catalysed transesterification process is more suitable for waste or unrefined oils, but it has not gained as much attention as the base catalysed transesterification due to its slower reaction rate and high methanol to oil molar ratio requirements [42]. The mechanism of the acid catalysed transesterification starts from protonation of the carbonyl group of triglyceride and generates a carbocation intermediate [43,44]. Acid catalysed transesterification reaction can be carried out in both homogeneous and heterogeneous systems. Generally, homogeneous acid catalysed transesterification is catalysed by BrØnsted acid such as sulphuric acid and hydrochloric acid [44]. During the process of transesterification of triglycerides by homogeneous acid, the triglycerides are converted to biodiesel and glycerol.

During the process of transesterification of triglycerides by homogenous acid catalyst, a glycerol layer will be formed and result in a loss of the catalyst [45]. High yields of alkyl esters are obtained by using acid catalysts, but the reaction is slow whereby reaction temperature above 100 °C and more than 3 h are required to reach the complete conversion [46]. Lee et al. [43] reported that the most common acid catalysed transesterification reaction using sulphuric acid requires a reaction temperature of 65 °C and more than 50 h to reach complete conversion of soybean oil with a methanol/oil molar ratio of 30:1.

On the other hand, great efforts have been made by the researchers to explore the use of solid acid catalyst in heterogeneous catalyst system to produce biodiesel [47]. It is believed that solid acid catalysts have strong potential to replace liquid acid catalyst due to their insensitivity to free fatty acid content, easy separation of catalysts from the reactant medium as well as reduce the corrosion problem even with the presence of acid species [47]. Heterogeneous acid catalysed transesterification can be carried out by using a solid acid catalyst such as Fe–Zn double metal cyanide [42], Zirconium oxide or Titanium oxide [47]. These solid catalysts consist of a mixed oxide, which promotes the transesterification reaction without catalyst loss at a higher reaction temperature, and pressure. Jitputti et al. [48] reported that at least 90% of methyl esters is obtained from the transesterification reaction of crude palm kernel oil with methanol in the presence of a solid acid catalyst of 3 wt% of SO_4^{2-}/ZrO_2. The experiment was performed at the temperature of 200 °C and pressures of 50 bar. Bournay et al. [47] conducted experimental studies to determine the methyl esters and glycerol content produced from rapeseed oil by the heterogeneous catalysed transesterification process. The heterogeneous acid catalyst used in this experimental study consists of a mixed oxide of zinc and aluminium and the reaction was performed at higher temperature and pressure. The glycerol content was determined by gas chromatography using the European standard test method. The authors noted the glycerol obtained is at least 98 wt% pure.

3.1.2. *Base catalysed transesterification*

The base catalysed transesterification reaction proceeds faster than the acid catalysed reaction [44]. Base catalysts such as alkaline metal alkoxides and hydroxides, sodium or potassium carbonates are used in base catalysed transesterification process.

Table 2
Advantages and disadvantages of various types of catalyst used in transesterification reaction. (modified from Ref. [41]).

Types of catalyst		Advantages	Disadvantages
Homogeneous base catalyst	• NaOH • KOH	• Very fast reaction rate • The reaction can occur at mild reaction condition and less energy intensive • High conversion can be achieved • These catalysts are widely available and economical	• The usage limits for oil with less than 0.5 wt% FFA • Soap will be formed if the FFA content in the oil is more than 2 wt% • Excessive soap formation will reduce the biodiesel yield and cause the problem during the product purification
Heterogeneous base catalyst	• CaO • MgO	• Relatively faster reaction rate than acid catalysed transesterification • The reaction can occur at mild reaction condition and less energy intensive • Easy separation of catalyst from product • High possibility to reuse and regenerate the catalyst	• Sensitive to FFA content in the oil due to its basicity property • Soap will be formed if the FFA content in the oil is more than 2 wt% • Excessive soap formation will decrease the biodiesel yield and cause the problem during product purification • Leaching of catalyst active sites may result to product contamination
Homogeneous acid catalyst	• H_2SO_4 • HCl	• Insensitive to FFA content and water content in the oil • Preferred-method if low-grade oil is used • Esterification and transesterification can occur simultaneously • The reaction can occur at mild reaction condition and less energy intensive • More economical than base catalysed process	• Very slow reaction rate • Required high reaction temperature and high molar ratio of alcohol to oil • Corrosive catalyst such as H_2SO_4 used can lead to corrosion on reactor and pipelines • Separation of catalyst from product is problematic
Heterogeneous acid catalyst	• ZrO_2 • TiO_2 • SnO_2 • Zeolite	• Insensitive to FFA content and water content in the oil • Preferred-method if low-grade oil is used • Esterification and transesterification occur simultaneously • Eliminate the washing step of biodiesel • Easy separation of catalyst from product • High possibility to reuse and regenerate the catalyst • Reduce corrosion problem	• Complicated catalyst synthesis procedures lead to higher cost • Required high reaction temperature, high alcohol to oil molar • Ratio and long reaction time are required. • Energy intensive • Leaching of catalyst active sites may result to product contamination
Enzyme	• *Mucor miehei* (Lipozym IM 60) • *C. antarctica* (Novozym 435) • *Bacillus subtilis*	• Insensitive to FFA and water content in the oil • Preferred-method if low-grade oil is used • Transesterification can be carried out at a low reaction temperature, even lower than homogeneous base catalyst • Only simple purification step is required	• Very slow reaction rate, even slower than acid catalysed • transesterification • High cost • Sensitivity to alcohol, typically methanol that can deactivate the enzyme

Alkaline metal alkoxides are the most active catalysts due to shorter reaction times (30 min) is required and high yields (>98%) are obtained at a low molar concentration (0.5 mol%) is applied [49]. Schuchardt et al. [49] and Demirbas [50] reported the mechanism of base catalysed transesterification process of vegetable oils. The process starts with the reaction of the base with the alcohol, producing an alkoxide and the protonated catalyst. The nucleophilic attack of the alkoxide at the carbonyl group of the triglyceride generates a tetrahedral intermediate, from which the alkyl ester and the corresponding anion of the diglyceride are formed. The latter deprotonates the catalyst can react with a second molecule of alcohol and starts another catalytic cycle. Diglycerides and monoglycerides are then converted by the same mechanism to a mixture of alkyl esters and glycerol.

Lee et al. [43] reported that homogeneous base catalysed transesterification process is fast and less methanol (5–15:1 methanol/oil ratio) as well as a lower reaction temperature (60–75 °C, around the reflux temperature of methanol) are needed. Nearly complete conversion (90%) is usually achieved within 2–6 h depending on the catalyst. Vicente et al. [51] conducted experimental studies to compare the biodiesel yield and glycerol content of the homogeneous base catalysed transesterification of sunflower oil reaction made of different basic catalysts such as sodium methoxide, potassium methoxide, sodium hydroxide and potassium hydroxide. All the reactions were carried out under the same experimental conditions: reaction temperature of 65 °C with a 6:1 M ratio of methanol to oil and 1% of basic catalyst by weight of vegetable oil. The total glycerol content of 0.0793, 0.0652, 0.780 and 0.1280 wt% is obtained from the transesterification of sunflower oil catalysed by sodium methoxide, potassium methoxide, sodium hydroxide and potassium hydroxide respectively.

In addition, base catalysed transesterification can also be carried out in heterogeneous system whereby a solid catalyst is used. Macedo et al. [52] investigated the heterogeneous base catalysed transesterification from soybean oil. The basic catalysts, Al_2O_3–SnO and Al_2O_3–ZnO, are used in the reaction and their effectiveness is examined. The biodiesel yields achieved was about 80% of soybean oil after 4 h at the reaction temperature of 60 °C by using 5 wt% of catalyst. Vyas et al. [53] conducted experimental study to examine the biodiesel conversion of the transesterification reaction of Jatropha oil with methanol. 6 wt% of Alumina loaded with potassium nitrate was used as a solid base catalyst for the reaction. The biodiesel conversion of 84% was achieved at a reaction temperature of 70 °C, reaction time of 6 h and the molar ratio of methanol to Jatropha oil (12:1).

3.1.3. *Enzymatic catalysed transesterification*

Presently, enzymatic catalysed transesterification have been developed to overcome the problems associated with acid and base catalysed transesterification. Major problems with acid and base catalysed transesterification are high-energy requirements,

potential pollution to the environment and difficulties in the recovery of the catalyst and glycerol [54]. Enzyme catalysis proceeds with high purity by-product (glycerol), easy recovery of product, mild reaction condition requirement and catalyst can be reused [55]. However, there are major drawbacks of enzyme catalysis when implemented in industrial scale such as high cost of enzyme, slow reaction rate and enzyme deactivation [56]. Generally, enzymes are effective biocatalysts due to high substrate specificity property, functional group specificity and stereo specificity in aqueous medium. Biocatalysts have become increasingly important for industry as they have a high specific activity and a low impact on the environment [57]. Biocatalysts such as lipases are widely employed to catalyse hydrolysis, alcoholysis, esterification and transesterification of triglycerides [58]. Lipases are also used as catalysts for the reactions involving biomodification of triglycerides [59]. Novozym 435 was reported to be an effective lipase catalyst for biodiesel production [60]. Tamalampudi et al. [61] have investigated the production of biodiesel from Jatropha oil through enzymatic catalysed transesterification. The reaction is catalysed by the whole cell of lipase producing Rhizopus oryzae immobilized onto biomass support particles. The yield of methyl ester achieved was 80% after 60 h by using 4% of Rhizopus (by weight of oil) in the presence of 5% (v/v) water, methanol to oil ratio of 1:1 and reaction temperature of 30 °C. Jeong and Park [62] performed enzymatic catalysed transesterification of rapeseed oil by using Novozym 435 as a catalyst. The conversion efficiency was more than 76% in the presence of 5% (w/w) of Novozym, methanol to oil molar ratio of 3 at 40 °C in 24 h.

3.2. Saponification

Glycerol formed in large quantities as the by-product in the process of saponification of triglycerides in the production of free fatty acids and fatty esters. Saponification reaction is the hydrolysis of fat and oils (triglycerides) with alkali resulting in two products, which are salts of fatty acid (also called soap) and glycerol as presented in Fig. 2 [61]. During the saponification process, the alkali break the ester bond and releases the glycerol and soap of alkali metal. Three molecules of soap are formed and the interaction between one molecule of triglyceride and three molecules of alkali liberates one molecule of glycerol. Caustic alkali react spontaneously with free fatty acid and soap is formed immediately under the condition of adequate mixing and agitation [63]. The soap is filtered and the filtrate contains 35% glycerol, free alkali, soluble soap, some NaCl as well as suspended impurities. This saponification reaction forms the foundation of the soap-making industry and is the basis of the commercial soap-making process. The process of soap manufacture of fat and oils usually yields glycerol to about 10% of the value of the soap formed [64]. Consequently, better reaction routes and condition with efficient glycerol purification are required to maximize the economics of large scale of soap production.

3.3. Hydrolysis

Fat and oils can be hydrolyzed into corresponding fatty acid and glycerol. Hydrolysis is the reversible reaction whereby a molecule of steam breaks a fatty acid off the glycerine backbone of a triglyceride, resulting in a free fatty acid and glycerol [65]. The reaction can be represented by the following equation as shown in Fig. 3. Hydrolysis reaction is similar to saponification reaction, but fat and oil reacts with water to yield a fatty acid and glycerol in this case. During the hydrolysis reaction, a light phase which contains fatty acid and the heavy phase, which consists of glycerol and impurities are obtained [65]. This glycerol-rich solution is called sweetwater. The glycerol by-product must be withdrawn continuously to force the reaction to completion. During the hydrolysis reaction, each molecule of fat and oils will yield one mole of glycerol and three moles of fatty acid [63]. The weight relationship for the reaction is hydrolysis of 100 g fat and oil with 6.1 g of water will produce 95.7 g of fatty acid and 10.4 g of glycerol [66]. Glycerol is recovered from the hydrolysates of fat and oils and contains a mixture of glycerine, water and impurities such as free fatty acid. Thus, the need for high purity glycerol requires removal of impurities from the solution through the purification techniques.

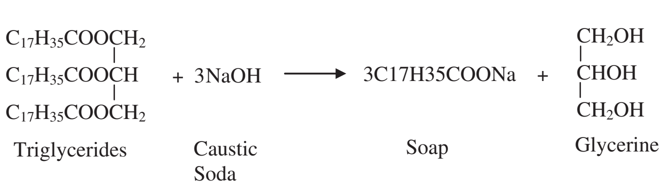


Fig. 2. Saponification reaction.

4. Crude glycerol from various production processes

Crude glycerol is the glycerol produced immediately after the reaction and the impurities such as used catalyst and excess of alcohol being found in the glycerol phase [67]. Crude glycerol contains impurities such as alcohol, spent catalyst, ash, water, and fatty acid that barely differs from crude glycerol in their physical properties. The appropriate composition of a typical crude glycerol derived from transesterification, saponification and hydrolysis reaction of fat and oils is given in Table 3. Crude glycerol has high salt and free fatty acid content as well as substantial colour (yellow to dark brown) [13]. The crude glycerol produced from transesterification, saponification, and hydrolysis is of low quality due to its composition. Thompson and He [36] reported that crude glycerol from biodiesel production from various feedstocks is generally between 60% and 70% (wt) glycerol. Jain [68] found that the glycerol-rich solution produced from the saponification reaction contains 35% (wt) crude glycerol. Amin et al. [2] stated that sweetwater (glycerol-rich solution) produced from the hydrolysis reaction contain 15% (wt) of glycerol and will be concentrated to crude glycerol with 80% (wt) purity.

Further pure glycerol has numerous industrial uses and it is an important industrial feedstock in food, drug and cosmetic industries. The applications of crude glycerol are highly limited due to the presence of the salt and impurities and its fuel value is also

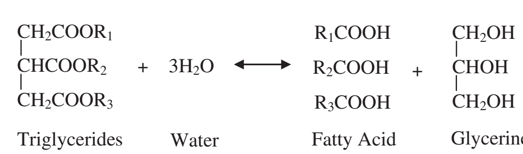


Fig. 3. Hydrolysis reaction.

Table 3
Composition of the crude glycerol derived from transesterification, saponification and hydrolysis reaction [36,68].

Component	Transesterification (%)	Saponification (%)	Hydrolysis (%)
Glycerol	75	83–84	88–90
Ash	10	8.5–9.5	0.7–1.0
Water	10	6–7	8 - 9
Mong (Matter organic non-glycerol)	5	3–4	0.7–1.0
Tmg (Trimethylene glycol)	1	0.1	0.2

marginal. The production of biodiesel generates millions of tons of crude glycerine waste per year and this amount is growing rapidly along with the dramatic growth of biodiesel industry [13]. Furthermore, the large quantity of impure glycerol produced from biodiesel industry and soap-making industry is available at very low prices because the production capacity of glycerol is far exceeding the market's requirement. This could reduce the commodity price of pure glycerol, which in turn destabilizes the market for oleochemical [69]. Thus, effective cost purification and refining technologies to purify crude glycerol to USP grade are required before it can be rendered suitable for industrial feedstocks for the production of value-added products.

5. Purification of crude glycerol

The quality of existing hydrolysed and biodiesel-derived glycerol is poor and unsuitable to be used as the feedstocks for further application as well as caused problems of disposal in biodiesel plant. Thus, purification is required to convert crude glycerol to a usable state, which has met the purity requirements for existing or emerging uses. Different methods have been used to purify crude glycerol such as distillation, filtration, chemical treatment, adsorption (using activated carbon), ion-exchange (using resin), extraction, decantion and crystallization whereby each of the purification techniques uses different properties of crude glycerol [70]. During the crude glycerol purification process, two or more purification methods are combined in order to achieve high effectiveness of purification. However, all the purification methods required a good understanding of the chemical and physical properties of materials involved. The combination of alcohol recovery by distillation as well as salt removal by ion-exchange resin and adsorption using activated carbon seems to be the common purification pathway [70].

Distillation is the most commonly practiced methods for purifying crude glycerol. Distillation is generally carried out to remove water and methanol based on the boiling point during glycerol purification. Distillation is also a simple and efficient method to purify crude glycerol with high contents of salts and matter organic non-glycerol (MONG). Yong et al. [71] reported that the purification of crude glycerol by simple distillation at 120–126 °C yield around 141.8 g glycerol/kg of glycerol residue (~14% yield) at an acceptance purity of 96.6% glycerol. The other characteristics of distilled glycerol were 0.03% of ash, 1% of water, 2.4% of matter organic non-glycerol (MONG) and pH 3.5. The authors also stated that the optimum pH for the distillation was <5 in which foaming was obviated. In general, distillation process offers: small to large-scale continuous operation, low cost of chemicals, adaptability of the process to suit varying qualities of crude and finish products [72]. However, the distillation of crude glycerol is an energy intensive process due to high specific heat capacity of glycerol that leads to a high-energy input requirement for vaporization and create thermal decomposition [71].

The crude glycerol can also be purified by ion-exchange method. Ion-exchange is a method for the removal of impurities, colour and odour through exchanging an ion from ion-exchange material [73]. This technique consumes small quantities of water for the separation of the salt from crude glycerol and it does not require the vaporization of glycerol. Isahak et al. [6] experimented the use of resin type Amberlite IRN-78 and Amberlite 200 to purify crude glycerol and investigated the effectiveness of resin. They performed the experiments by column technique, where the ion-exchange resins were placed in a vertical column forming a bed. The glycerol samples obtained after purification were analysed using High Performance Liquid Chromatography (HPLC). The chromatograms for the purified sample showed a single glycerol peak with a very smooth base line that matched to the pure glycerol profile. These results indicated that the impurities such as inorganic salts and free ions have been removed when the ion-exchange resin method was applied.

Besides, another possible purification method is pure of chemical (acid protonation) and physical treatment (filtration). For chemical treatment, the crude glycerol fraction can be reacted with acid to convert the alkoxide salts to the corresponding alcohol and the fatty acid carboxylate salts to the corresponding free fatty acid. The resulting free fatty acid can then be removed by extraction or decantion. Ooi et al. [4] reported that chemical treatment at low pH could reduce the ash content in the purified crude glycerol by using 6% (v/v) sulphuric acid. Hazimah et al. [74] recovered glycerol from the glycerol pitch by the combined process of chemical and physical treatment. High purity glycerol (~99.1% −99.8% (w/w)) with low contaminants (0.11–0.80% (w/w) water, 0.054% (w/w) ash and 0.56% (w/w) soap) was obtained. Kongjao [75] reported that high content of ash, water and MONG was successfully removed by using the combined approach of chemical and physical treatment with solvent extraction. High purity level of glycerol (~93.34% (w/w)) with low contaminants (0.00045% (w/w)) ash and 5.16% (w/w) of MONG was obtained at pH 1. Purification of crude glycerol by the approach of combined chemical and physical treatment offers: easy in operation, low operating cost and high efficiency.

6. Glycerol to value-added products

Glycerol is a major byproduct produced from oleochemical industry especially large surplus of glycerol formed as a by-product during the biodiesel production. The availability of glycerol will increase in future due to the remarkable growth of the biodiesel production worldwide. As the existing glycerol supply and demand market is tight and cannot accommodate the excess amounts of glycerol generated from biodiesel production, the flood of glycerol has created a glut in the glycerol market [76]. Thus, new markets or new applications of glycerol such as converting it into value-added products would have to be explored. Glycerol is a highly functionalized molecule compare to petro-chemically produced hydrocarbons, thus, a large number of value-added chemicals can be produced from glycerol via various types of chemical reactions [77]. For instance, catalytic oxidation of glycerol leads to the formation of various compounds such as dihydroxyacetone and glyceraldehydes [78]. Glycerol is used as the raw material in the production of dendrimers, hyper-branched polyester and polyesters that have a high surface area to volume ratio and numerous end groups for functionality [79].

6.1. 1,3-propanediol

1,3-propanediol is a simple organic chemical and it has a variety of applications in the production of polymers, cosmetics, foods, lubricants and medicines [80]. The production of 1,3-propanediol is limited and the costs are higher, thus, glycerol has become an attractive feedstock for the production due to its lower prices and present in abundance [81]. 1,3-Propanediol can be produced from glycerol via the following reactions such as fermentation, dehydroxylation and hydrogenolysis.

Glycerol serves as the feedstock for the production of 1,3-propanediol by fermentation. This process takes place in two-step enzymatic reaction sequence: glycerol dehydratase first catalyses the conversion of glycerol to 3 hydroxypropionaldehyde (3-HPA) and water. 3-HPA is then reduced to 1,3-propanediol by an NADH dependent 1,3-propanediol dehydrogenase [82]. Mu et al. [83] conducted experimental studies to produce 1,3-propanediol from

crude glycerol derived from methanolysis of soybean oil. Shake-flask and fed-batch fermentations were performed by *Klebsiella pneumoniae* to produce 1,3-propanediol using both pure glycerol and crude glycerol. The productivity of 1,3-propanediol from crude glycerol was found to be 1.7 g l^{-1} h^{-1}. Furthermore, It was shown that 51.3 g/l of 1,3-propanediol concentration was produced by crude glycerol from alkali-catalysed methanolysis of soybean oil, which was comparable to that of 53 g/l on crude glycerol derived from a lipase-catalysed process. Papanikolaou et al. [84] investigated the fermentation of glycerol in batch and continuous cultures of a newly isolated *Clostridium butyricum* strain. For both types of cultures, the conversion yield obtained was around 0.55 g of 1,3-propanediol formed per 1 g of glycerol whereas the highest 1,3-propanediol concentration, achieved during the single-stage continuous cultures was 35–48 g l^{-1}.

Besides, 1,3-propanediol also can be obtained through the selective hydrogenolysis of glycerol in the presence of a catalyst and hydrogen [82]. Selective hydroxylation technique selectively transforms the middle hydroxyl group of glycerol into a tosyloxyl group and then removes the transformed group by catalytic hydrogenolysis [81]. Nakagawa et al. [85] studied the hydrogenolysis of glycerol to 1,3-propanediol in an aqueous medium catalysed by Rhenium-oxide-modified to support iridium nanoparticles on silica. The result showed that selectivity to 1,3-propanediol at an initial stage reached 67 ± 3% and the yield of 1,3-propanediol reached 38% at 81% conversion of glycerol. Werpy et al. [86] conducted the hydrogenolysis of glycerol over Ni/Re catalyst. The result showed that a mixture of 44% 1,2-propylene glycol, 5% of 1,3-propylene glycol and 13% of ethylene glycol was obtained.

The glycerol dehydroxylation approach consists of three steps: acetalize the glycerol with benzaldehyde, tosylation of the unprotected hydroxyl group of the acetalized glycerol (to transform it into a good leaving group) and detosylation preceeded (yield 1,3-propanediol) [87]. This dehydroxylation reaction is to be done with molecular hydrogen in the presence of a transition metal catalyst. Korolev et al. [88] investigated glycerol dehydroxylation on a Raney cobalt catalyst in hydrogen. It was found that with an increase in temperature from 1400 °C to 200 °C at a hydrogen pressure of 30 MPa, glycerol conversion increases from 14% to 97%. The glycerol is completely converted in 20 h, and the yield of 1,2-propanediol is 40%.

6.2. Acrolein

Acrolein, also known as 2-propenal or acrylic aldehyde is the simplest unsaturated aldehyde [80]. It is used as intermediate for the synthesis of acylic acid and acrylic acid esters, as a slimicide in the manufacture of paper and as a microbiocide in oil wells. Acrolein can be produced from glycerol via the dehydration process with the presence of the catalyst [89]. Alhanash et al. [89] demonstrated the dehydration of glycerol to acrolein in the gas-phase process with the presence of Cs heteropoly salt as the catalyst. This reaction takes place at the reaction temperature of 275 °C and a pressure of 1 bar. The result showed that the catalyst exhibits high initial activity with a glycerol conversion of 100% at 98% acrolein selectivity. Watanabe et al. [90] produced acrolein from glycerol in hot-compressed water using a batch and a flow apparatus. They reported that the rate constant of acrolein decomposition had been always higher than that of acrolein formation, which could be overcome by adding acid catalyst. The result showed that 74 mol% of acrolein yield and 81% of its selectivity was obtained with acid catalyst in a supercritical condition of 673 K and 34.5 Mpa. Bub et al. [91] investigated the gas phase dehydration of glycerol to acrolein. The dehydration of glycerol can be carried out at 300 °C with a Zr as catalyst. The conversion of glycerol to acrolein is 72% when feed made of an aqueous an aqueous solution of glycerol is used.

6.3. Hydrogen

Glycerol can be converted into hydrogen through the variety of the following processes: steam reforming, partial oxidation, autothermal reforming [80]. The catalytic steam reforming is a high temperature endothermic process, which uses a catalyst to react the glycerol with water to produce hydrogen. The catalytic steam reforming of glycerol to produce hydrogen occurs in three steps: occur first through glycerol dehydrogenation, CO bonded onto the catalyst surface, which could then undergo desorption and followed by water–gas-shift or methanation [92]. Wang [93] studied thermodynamic properties of glycerol reforming for hydrogen production. The optimal conditions for hydrogen production from glycerol were found to be at a temperature of 925–975 K and a water/glycerine ratio of 9–12 at atmospheric pressure. At 925 K and a water/glycerine ratio of 12 under atmospheric pressure, the maximum number of 6.2 mol of hydrogen can be produced with per mole of glycerine.

In addition, hydrogen can be produced from glycerol by the process of partial oxidation. Partial oxidation is the process in which a substrate reacts with oxygen at sub-stoichiometric ratios [80]. Wang et al. [94] studied the thermodynamics of glycerol partial oxidation for hydrogen production by Gibbs free energy minimization method. The optimum conditions for hydrogen production are identified as follows: reaction temperatures between 1000 Kand 1100 K and oxygen-to-glycerol molar ratios of 0.4–0.6 at 1 atm, complete conversion of glycerol with 78.93–87.31% yield of hydrogen could be achieved in the absence of carbon formation under the optimal conditions. The further autothermal reforming process combines the effect of partial oxidation and steam reforming by feeding fuel, air, and water together in the reactor [80]. Swami and Abraham [95] conducted autothermal reforming at a steam-to-carbon ratio of 3 and an oxygen-to-carbon ratio of 0.3 in the range of reaction temperature of 550–850 °C by using the Pd/Ni/Cu/K as the catalysts. The results showed that the hydrogen yield during autothermal reforming was greater than that of steam reforming, though the hydrogen yield for both reactions increased with temperature.

6.4. Industrial applications

Glycerol is a valuable by-product as it has a wide range of industrial applications. At present, glycerol has over two thousand different applications [96], especially in pharmaceuticals, personal care, foods and cosmetics, as shown in Fig. 4. Glycerol is a nontoxic, edible, biodegradable compound, thus, it will provide important environmental benefits to the new platform products. Glycerol is widely used in the manufacture of drugs, medicine and pharmaceuticals for the purpose of dissolving drugs, giving the pills humidity and increasing the viscosity of liquid drugs. It is used in cough syrups, ear infection medicines, as a carrier for antibiotics and antiseptics and plasticizers for medicine capsules [98]. Glycerine is an excellent solvent of iodine, bromine, phenol, tannins, alkaloids, and mercury chloride [99]. Glycerol is used in personal care formulations, mainly as a means of providing lubrication, improving smoothness, and as a humectant and moistener in many skin and hair care products where moisturization is desired [98]. Glycerol is the major ingredient in toothpastes to prevent hardening and drying out in the tube, thus, toothpastes are estimated to make up almost one-third of the personal care market for glycerol [7].

In the food and beverage industry, glycerol acts as a solvent, sweetener and preservative agent. It is normally ingested in

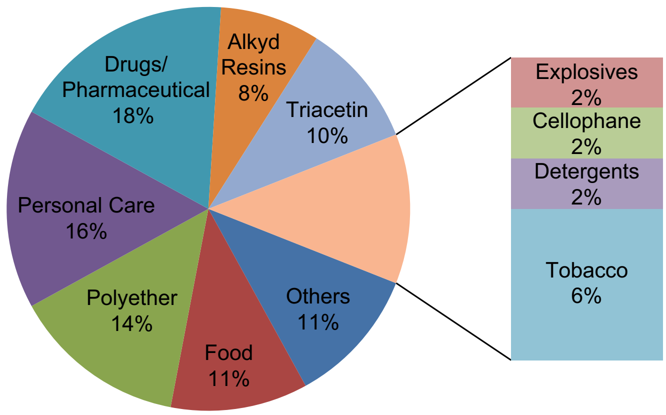


Fig. 4. Glycerol industrial applications [97].

Table 4
Production rates and prices of glycerol on 2008.

Characteristics	Value	Units	References
Biodiesel production in U.S.	5.2×10^9	Ib/year	[102]
Crude glycerol from biodiesel production in U.S.	5.2×10^8	Ib/year	[102]
World production of glycerol	3.8×10^9	Ib/year	[103]
Crude glycerol from biodiesel production	3.8×10^8	Ib/year	[103]
Price of crude glycerol	3.5–10	cents/Ib	[104]
Price of refined glycerol	40–50	cents/Ib	[103]

manufacturing extracts of tea, coffee, ginger and other vegetable substances. It is also used as a softening agent in bread, cakes, meats, cheese and candy. There is no objection to the use of glycerol in food and beverage industry, provided it is purified and quantity suitable for food use [99]. Glycerol can be used to preserve the freshness of tobacco and regulate the moisture content of tobacco in order to eliminate the unpleasant irritating taste [98]. In paper production, glycerol is used as a plasticizer and lubricant. Glycerol is used in the textile industry in sizing, lubricating and softening yarn and fabric [10].

7. Economic evaluation

The worldwide production of glycerol is estimated to be around 750,000 t per year, almost entirely produced from triglycerides; only 12% of the worldwide production is made synthetically [100]. The market of glycerine is volatile and its prices are strongly dependent on the supply. In the near future, the supply of crude glycerol might be greatly dependent on the biodiesel plant due to the growth of biodiesel plant whereby glycerol is produced as the by-product. With an estimated capacity of biodiesel of 12 M metric tons per year in 2010, 1.2 M metric tons of glycerol are produced and becoming a bulk renewable feedstock [100]. The saturation of glycerol in the market caused the prices of glycerol decreasing continuously to about $0.05 Ib^{-1} [76,101]. Table 4 summarizes the production rates and prices of the glycerol worldwide and in the U.S.

Although the glycerol market demand is low in the U.S, but the rising standard of living in developing countries provides the greatest opportunity for growth in the traditional uses of glycerine [105]. Asia is the largest producer and consumer of refined glycerine. In 2007, Asia accounted for 44% and 35% of world production and consumption, respectively [106]. Western Europe is the second-largest producer and consumer of refined glycerine, accounting for nearly 35% and 28% of world production and consumption, respectively while North America was the third-largest market in 2007 [105]. These three regions accounted for nearly 91% of world production and 82% of world consumption in 2007 [106].

8. Conclusions

From the foregoing the following conclusions are made:

1. Although glycerol can be produced through routes (saponification, hydrolysis, esterification and the transesterification), but its mass production is currently achieved through the transesterification process.
2. It was noted that the production of every 10 kg of biodiesel via the transesterification process yields approximately 1 kg of crude glycerol.
3. It was found that the nature of the raw material and catalyst used during the transesterification process influences the purity and quality of the biodiesel and glycerol.
4. It was reported that the present glycerol market is low due its abundance and presence of impurities in the crude glycerol.
5. It was found that several purification techniques are being developed to purify glycerol to commercial, with the use of activated carbon or ion-exchange resins being among the prospective for the achievement of high-grade glycerol.
6. Finally, the achievement of high-grade glycerol products will help in raising the standards for biodiesel activities.

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